Water Monitoring for Per- & Poly-Fluoroalkyl Substances Quality Assurance Project Plan (QAPP)

For Programs Implemented by the Kentucky Department for Environmental Protection

Kentucky Division of Water
Kentucky Department for Environmental Protection
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LIST OF ACRONYMS

AFFF - Aqueous Film-Forming Foam

COA – Certificate of Analysis

COC - Chain of Custody

CPR - Cardiopulmonary Resuscitation

CWA - Clean Water Act

DEPS - Division of Environmental Program Support

DO - Dissolved Oxygen

DOW - Division of Water (KY)

DQI - Data Quality Indicator

DQO - Data Quality Objective

EPA – Environmental Protection Agency (U.S.)

GIS - Geographic Information System

GPS - Global Positioning System

HA - Health Advisory

HAZWOPER - Hazardous Waste Operations and Emergency Response

HDPE - High-density polyethylene

KDEP (Department) – Kentucky Department for Environmental Protection

K-WADE – Kentucky Water Assessment Data for Environmental Monitoring

LIMS - Laboratory Information Management System

LOD - Limit of Detection

LOQ - Limit of Quantitation

LOQAM - Laboratory Operations and Quality Assurance Manual

MCL - Maximum Contaminant Level

NIST - National Institute of Standards and Technology

NPDES - National Pollutant Discharge Elimination System

PFAS - Per- & Poly-Fluoroalkyl Substances

PFOA - Perfluorooctanoic acid

PFOS – Perfluorooctane sulfonate

QA - Quality Assurance

QAC – Quality Assurance Coordinator

QAO – Quality Assurance Officer

QAPP – Quality Assurance Project Plan

QA/QC – Quality Assurance Quality Control

QC – Quality Control

QMP – Quality Management Plan (KDEP, 2016)

RPD - Relative Percent Difference

SOP - Standard Operating Procedures

UCMR3 - Third Unregulated Contaminant Monitoring Rule

USGS - United States Geological Survey

WMB - Watershed Management Branch

WQB - Water Quality Branch

WQX – Water Quality Exchange

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1.0 PROJECT MANAGEMENT

1.1 Project Background and Overview

Water quality monitoring programs administered by the Kentucky Division of Water (DOW) provide a comprehensive monitoring plan for measuring and reporting on the health of the Commonwealth's freshwater resources. The programs are designed to meet numerous objectives, including Kentucky's responsibilities under the Clean Water Act (CWA) and additional state-specific goals. All monitoring programs are conducted under the guidelines laid out in the Quality Management Plan (QMP) of the Kentucky Department for Environmental Protection (KDEP). The QMP requires all programs that collect data to develop a Quality Assurance Project Plan (QAPP) to address the specific quality requirements that will ensure programs produce data of known and sufficient quality that are ultimately useable for their intended purposes.

Per- and poly-fluoroalkyl substances (PFAS) have been identified as contaminants of emerging concern. These compounds are ubiquitous and have been used since the 1940s for their ability to resist heat, oil, grease and water. The most common uses have been stain resistance for carpets, non-stick cookware, and aqueous film-forming foam (AFFF). These chemicals are persistent in the environment, and can bioaccumulate in organisms. There is evidence that exposure to PFAS chemicals may impact reproductive and developmental health, increase the risk for cancer, disrupt thyroid hormones, and affect the immune system (EPA, 2018). The United States Environmental Protection Agency (EPA) and many states are assessing the need to establish Maximum Contaminant Levels (MCLs) for PFAS exposure in drinking water.

The EPA's Third Unregulated Contaminant Monitoring Rule (UCMR3) examined the occurrence of six different PFAS in drinking water nationwide. The finished water from all community water systems in the United States serving more than 10,000 people, and a representative sample of 800 systems serving less than 10,000 people, were sampled. In Kentucky, 121 water systems with 165 drinking water sources were monitored under this rule for the occurrence of PFAS. Nationally, 4% of public water systems reported detections of PFAS while Kentucky had detections in 1.82% of sampled sources. Detections in drinking water were associated with numerous potential sources of PFAS, including industrial sites, areas where fire training with AFFF occurred, and wastewater treatment facilities (Interstate Technology Regulatory Council, 2018).

On May 19, 2016, the EPA issued drinking water lifetime health advisories (HA) for two PFAS compounds, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). The HA level is 70 ng/L for PFOA, and 70 ng/L for PFOS. The EPA further recommends that when these two chemicals co-occur at the same time and location in a drinking water source, a conservative and health-protective approach would be to compare the sum of the concentrations ([PFOA] + [PFOS]) to the HA (70 ng/L). Lifetime health advisories are not drinking water standards (MCLs or Treatment Technology) but may be used for developing local standards. In addition, the HA is being utilized as a screening level of public and private drinking water. The EPA is also proposing to use the HA as a remediation goal for PFAS-contaminated groundwater being used for consumptive purposes. The EPA has not established health advisories for the other PFAS at this time.

The Kentucky Department for Environmental Protection's (KDEP) 2019 examination of the occurrence of PFAS in a representative sample of Kentucky's public drinking water greatly expanded our knowledge of the occurrence of these chemicals. Samples of finished (treated) water were collected and analyzed from 81 community public drinking water treatment plants (WTPs), representing 74 public drinking water systems, over the course of four months. Sampling sites were chosen to represent surface water (43 WTPs) and groundwater (38 WTPs) supplies, urban and rural land-use influence, and varying sizes of populations served. Source waters for the WTPs sampled include each of Kentucky's major river basins, the main stem of the Ohio River and major aquifers in the state.

The population served by the WTPs sampled in that study account for approximately half the population in Kentucky on public water. Table 1.1 summarizes the PFAS analyzed in that study.

Table 1.1. PFAS analyzed in drinking water study

Analyte	Acronym	CAS Number
Perfluorobutanesulfonic acid*	PFBS	375-73-5
Perfluoroheptanoic acid*	PFHpA	375-85-9
Perfluorohexanesulfonic acid*	PFHxS	355-46-4
Perfluorononanoic acid*	PFNA	375-95-1
Perfluorooctanesulfonic acid*#	PFOS	1763-23-1
Perfluorooctanoic acid*#	PFOA	335-67-1
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6

^{*}Indicates PFAS analyzed in UCMR3

PFAS were detected at 41 of the 81 water treatment plants, the majority of which represent surface water sources. All detections of PFAS were below the EPA Health Advisory of 70 ng/L. One or more PFAS were detected at 31 surface WTPs (72%) and 10 groundwater WTPs (26%). The most frequently detected analyte was PFOS, which was followed by PFOA. The highest concentration of any PFAS detected was HFPO-DA at 29.7 ng/L. ADONA was not detected in any samples. All samples were collected by KDEP staff and were analyzed by the Department's Division of Environmental Program Support (DEPS) laboratory (KDEP, 2019).

The Department's evaluation of drinking water for PFAS occurrence was the first proactive step to characterize the risk of exposure associated with these chemicals. That study included numerous water systems that do not currently utilize treatment technology to remove these chemicals. Therefore, those results are an indicator of ambient PFAS concentrations within portions of those source waters. This is especially true for the drinking water systems that use groundwater as their sources because treatment requirements are not as stringent.

The next phase of this proactive approach is a broader evaluation of Kentucky's water resources for the occurrence of PFAS. Water resources include all of the waterways, waterbodies and aquifers in the Commonwealth that contribute to drinking water and may be used for commercial, industrial, and recreational activities. This will expand our knowledge on the occurrence of PFAS in Kentucky's water resources. Additionally, it will alert the Department to any potentially problematic areas that may require further investigation.

1.2 Project / Task Organization

General roles and responsibilities are common throughout all DOW monitoring programs (<u>Figure 1.1</u>). Personnel responsible for program- or project-specific roles are described.

1.2.1 Department for Environmental Protection (KDEP) Roles and Responsibilities

Quality Assurance Manager, Department for Environmental Protection (KDEP):

Reviews the QAPP and may require language or content be added to ensure the QAPP meets the objectives
of the QMP.

Quality Assurance Officer (QAO), Division of Water (DOW):

- Maintains most current QAPPs, manages QAPP locations on network drives, and archives historic QAPPs.
- Provides technical support and reviews and approves quality assurance (QA) products.

^{*}Indicates PFAS for which EPA has issued a Health Advisory

- Communicates with EPA Project Officers and QA personnel on QA issues and activities.
- Division authority on EPA QA regulations and QA guidance.
- Authority on division QA policy and ensures staff understand and follow the KDEP QMP.
- Ensures that all personnel involved in environmental data collection have access to any training or QA
 information needed to be knowledgeable in QA requirements, protocols, and technology. The QAO will
 coordinate this training if needed.
- Provides technical assistance for data quality issues.

Manager, Water Quality Branch (WQB):

- Supervises branch personnel, oversees program development, coordinates branch resources, and monitors the overall implementation of programs and projects.
- Communicates with the QAO, program supervisors, and staff on branch/division needs.
- Understands Division QA policy and ensures staff understand and follow the policy.
- Ensures Standard Operating Procedures (SOPs) are developed and updated.
- Ensures that all WQB staff have access to any training or information needed to be knowledgeable in collecting quality data and QA requirements.
- Ensures the review of QA data.

Quality Assurance Coordinator (QAC), Water Quality Branch (WQB):

- Maintains the WQB environmental monitoring QAPP folder.
- Provides content review, and coordinates with other specialists in WQB to accomplish reviews.
- Coordinates activities of the WQB Quality Assurance and Quality Control (QA/QC) Work Group and briefs the WQB Manager.
- Attends DOW QA/QC meetings.
- Reports QA/QC activities to DOW QA Officer.
- Provides Interim QA Data Reports on all current projects.
- Coordinates the completion of annual PSPs and PMPs with program supervisors.
- Works with project coordinators to set up projects and trips in Kentucky Water Assessment Data for Environmental Monitoring (K-WADE).
- Tracks project activities and data entry through project data reports.

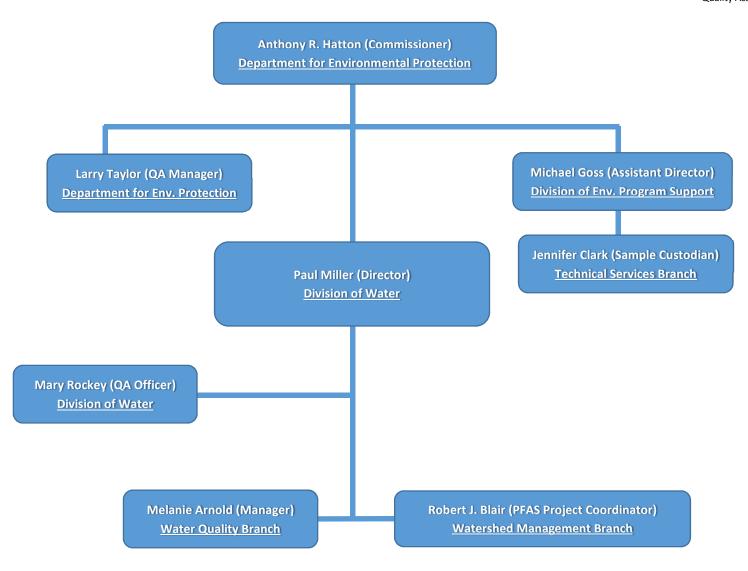


Figure 1.1. Organizational structure for PFAS monitoring project within the Kentucky Division of Water.

<u>Project Coordinator, Watershed Management Branch (WMB):</u>

- Serves in role of "Project Officer" in KDEP QMP.
- Ensures that QMP requirements are integrated into project designs.
- Supervises activities of project staff.
- Notifies management team about any staff training needs.
- Develops study plan to ensure that the project meets data quality objectives.
- Coordinates QA/QC activities and data verification.
- Ensures proper validation and verification of data according to QAPP requirements.
- Develops final project report.
- Understands division QA policy and ensures staff understand and follow the policy.
- Ensures project staff administer project in accordance with the QAPP and SOPs.
- Verifies all QA/QC review and project closeout procedures have been completed.
- Identifies sampling stations.
- Coordinates project field activities, data collection, data management and data curation.
 - Ensures data are collected and curated following guidance detailed in QAPP documents and SOPs.
 - o Reviews DEPS sample receipt confirmation emails against Chain of Custody (COC).
 - Reviews project files stored in K-WADE and network drives to ensure file storage is following QAPP requirements.
 - Reviews analytical data reports as they are provided to ensure data are meeting Data Quality Objectives
 (DQOs) and that data are being stored as described.
- Take corrective actions when data do not comply with DQOs.
 - Ensures that proper documentation, notes, and/or data flags are entered into K-WADE for data not meeting DQOs.
- Serves as Field Lead for activities completed in the field.
- Directs activities during field station visits according to project documentation and ensures all required data are entered on datasheet.
 - o Ensures instrument calibrations are performed following SOPs and all equipment functions properly.
 - Ensures proper handling and transport of all supplies and equipment during field activities.
 - o Completes sample COC for chemistry samples.
 - o Documents on datasheets any necessary deviations from established methods for all led activities.
- Data Finalization
 - Performs initial data review.
 - Ensures that activity data are entered into K-WADE following QAPP guidelines.
 - o Ensures all project documents follow standard naming conventions.
 - Ensures documents are stored on network drives and K-WADE.

Technical Staff – Division of Water:

- Aids in collection of all data under the supervision of the project coordinator.
- Must be familiar with QAPP and SOP.
- Performs QA/QC controls for completed field activities, when directed.
- Performs other specific tasks, if any, as described in the project work plan.

1.2.2 Division of Environmental Program Support

As a support facility the DEPS is responsible for performing water, sediment, and tissue chemical analyses. The DEPS follows guidance from their <u>Laboratory Operations and Quality Assurance Manual (LOQAM)</u>, which details personnel duties. The positions listed below are primarily responsible for ensuring that sample receiving guidelines and analytical methods are followed.

Assistant Director, Division of Environmental Program Support (DEPS):

The DEPS Assistant Director has the following responsibilities:

- Manages and oversees all lab operations.
- Oversees verification of analytical data and certifies results for release.

Sample Custodian, Division of Environmental Program Support (DEPS):

The DEPS Sample Custodian has the following responsibilities:

- Ensures all samples arrive at the laboratory properly labeled and preserved.
- Ensures COC procedures are properly followed.
- Ensures samples are assigned to proper laboratory section (inorganic/organic) for analysis.

1.3 Data Quality Objectives (DQOs) Process

1.3.1 Action Limits / Levels

The primary objective of this project is generating data to evaluate the occurrence and concentrations of PFAS in Kentucky's source waters. The design, data collection methods, and precision of laboratory analyses must be compatible with this objective and the decision processes regarding further PFAS-related initiatives. The Program Coordinator works with the DEPS laboratory Assistant Director to ensure that reporting limits are below health advisory levels or other relevant assessment thresholds.

1.3.2 Performance and Acceptance Criteria

The types of data collected for this project includes the following: water chemistry samples, *in situ* instantaneous physical/chemical data, and visual observations of site conditions.

Parameter-specific performance and acceptance criteria for data collected under this QAPP will be expressed using these Data Quality Indicators (DQIs): precision, representativeness, comparability, completeness, accuracy, sensitivity, and bias. The purpose of the DQIs defined below is to ensure that the data collected maintain tolerable levels of uncertainty for their intended use. Parameter-specific DQOs are described based on these DQIs (Tables 1.2-1.5). Any data that fall outside of the stated realms of acceptability will be flagged in all data reports. Ultimately, it will be the responsibility of the end user to determine if flagged data will be used.

Completeness

Completeness refers to the amount of valid data needed to evaluate PFAS occurrence. Completeness requirements will be determined based data acquisition sufficient to determine the presence or absence of PFAS in monitored locations, and concentrations of PFAS where present. Laboratory analytical reports for each monitored location will be sufficient to determine presence or absence of PFAS and the concentrations, where present.

Representativeness and Comparability

All project activities will follow the SOP to ensure representativeness and comparability with past and future data. Representativeness controls are usually described in SOPs and include guidelines such as sampling location criteria, sample collection protocols, and sensor placement for *in situ* multi-parameter probes. Where SOPs give procedural options, any deviations from primary or default procedural options must be noted. Furthermore, any deviations from SOPs must be documented.

 Table 1.2. Summary of data quality objectives for PFAS monitoring programs

Parameter	Representativeness and Comparability	Precision	Accuracy, Sensitivity, and/or Bias
Water PFAS Samples	Adherence to relevant SOP	Field duplicate samples will be collected at each monitoring station. A minimum of one monitoring station will be sampled in triplicate for each sampling day ($^{\sim}10\%$). Full acceptability of PFAS values from a sampling round will be based on criteria found in Table 1.5.	Adherence to relevant DEPS laboratory SOPs. Analytical accuracy and bias are monitored with reference samples and matrix spikes. Percent recovery is expected to be 90-110%. Field blanks, trip blanks and replicate samples will be used to monitor for contamination of supplies or improper handling.

Table 1.3. Summary of data quality indicators for *In situ* measurements in water quality monitoring programs

Parameter	Units	Representativeness and Comparability	Sensitivity	Precision, Accuracy, Bias
In situ Water Quality		Adherence to relevant SOPs. If duplicate readings are		Water quality meters must adhere to measurement ranges and sensitivities listed here and in Table 1.4
Meters		taken, a minimum of 10% RPD criterion will be applied		water quality meters must duffere to measurement ranges and sensitivities listed here and in Table 1.4
Temperature	°C	п	0.10°C	Adherence to relevant SOP and manufacturer specifications, periodic checks against NIST thermometer
Specific Conductivity	μS/cm	п	1 μS/cm	Adherence to relevant SOP and manufacturer specifications, calibrate at least weekly during use
pH	St. Units	п	0.01 units	Adherence to relevant SOP and manufacturer specifications, calibrate at least weekly during use
Dissolved Oxygen	mg/L	п	0.01 mg/L	Adherence to relevant SOP and manufacturer specifications, calibrate prior to each sampling trip (minimum)
% Saturation	%	п	1%	Adherence to relevant SOP and manufacturer specifications, calibrate prior to each sampling trip (minimum)
GPS	Desimal Degrees	II	0.00001°	Adherence to manufacturer specifications. North American Datum (NAD) 1983. Position accuracy of ±10 meters. Devices allowed to "Acquire
	Decimal Degrees		0.00001°	Satellites" for at least 30 seconds to ensure the most accurate coordinates are captured

Table 1.4. Water Quality Meter Measurement Ranges

Exo Probe	Range	
DO % Saturation	0 - 500%	
Dissolved Oxygen	0 to 50 mg/L	
рН	0 to 14 pH units	
Specific Conductance	0 to 100 mS/cm	
Temperature	-5 to 50°C	
Pro Plus and ProDss Probe	Range	

Pro Plus and ProDss Probe	Range
DO % Saturation	0-500%
Dissolved Oxygen	0-50mg/L
рН	0-14 pH units
Specific Conductance	0-200 mS/cm
Temperature	-5 to 70 $^{\circ}\text{C}$ (temp compensation for DO mg/L measurement -5 to 50 $^{\circ}\text{C}$

Table 1.5. Field Replicates Precision Acceptance Criteria

Sample Spread	Acceptance Criterion
All samples are ≥ 5x the LOQ	A relative percent difference (RPD) of 20%
1 of 3 samples is ≥ 5x the LOQ	An absolute difference \leq to the 2x LOQ ⁽¹⁾
All samples are < 5x the LOQ	An absolute difference ≤ to the 2x LOQ ⁽¹⁾
All samples are non-detect	Not Applicable – No Calculation Required

⁽¹⁾ If both samples are less than 5x the Limit of Quantitation (LOQ) and are also found to have an absolute difference of >2x LOQ, these data will be investigated further. If sufficient additional indicators of QA issues are found, the samples will be considered to have failed this QA check. Corrective action will be implemented as appropriate and outlined in this QAPP. All corrective actions must be reported in the final data report.

Precision, Accuracy, Sensitivity, and Bias

Precision, accuracy, sensitivity, and bias for activities will be evaluated based on the definitions below. These elements will be controlled through numerous performance requirements including adherence to sample and lab analysis SOPs, instrument maintenance and calibration requirements, quality control (QC) blanks and replicates, and laboratory QC samples. Specific SOPs outline the specifications for measurement instruments used in projects.

Precision – the measure of agreement among repeated measurements of the same property under identical or substantially similar conditions.

Accuracy – a measure of the overall agreement of a measurement to a known value.

Sensitivity – the capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest.

Bias – systematic or persistent distortion of a measurement process that causes error in one direction.

1.4 Special Training Requirements

1.4.1 Field and Laboratory Training Requirements

The project coordinator will ensure that staff have been appropriately trained for project activities. Project tasks will be performed by personnel trained in the pertinent SOPs. SOP training involves initial in-person instruction along with annual SOP reviews. Technical staff assisting with any field or laboratory tasks will be under the direct supervision of qualified personnel.

Project staff will meet the minimum qualifications for their job classification. Those who have never completed a particular field/laboratory activity are trained on proper collection procedures, and the training is recorded in the individual's training record. Field technical staff must review all SOPs relevant to the job duties outlined in their position description and receive training on-the-job and/or during formal training events from senior field support staff. Official training records are maintained by the Kentucky Personnel Cabinet and additionally in the state of Kentucky employee training tracking system (mypurpose.ky.gov). Water PFAS sampling, sample handling procedures, and *in situ* water quality meter usage/calibration training will occur on-the-job and/or through formal training events from senior field support staff.

Finally, SOPs include staff health and safety information, and field staff will be trained in the pertinent Worksite Hazards/Health and Safety Plans (DOWSOP03051, 2019). Because work is often performed in remote locations, field staff will be certified in first aid, CPR, blood borne pathogens, and HAZWOPER (OSHA 1910.120) with annual recertification completed as required. Training records are maintained in the state of Kentucky employee training tracking system (mypurpose.ky.gov).

1.4.2 Analytical Laboratory Training Requirements (DEPS)

The DEPS lab is accredited by <u>the National Environmental Laboratory Accreditation Program</u> (NELAP) and complies with all requirements, including training. Training and certification requirements for DEPS technical staff performing water sample analyses will follow guidelines in the DEPS LOQAM.

1.5 Documentation and Records

All field activity progress must be documented in traceable, clear, and concise records. In general, management of records will follow these principles:

- After initial data review, paper documents are scanned to PDF documents for storage on network drives and attachment to K-WADE station visits and/or projects.
 - o Electronic copies facilitate data entry and QA/QC tasks, as well as to serve as backups.
- Paper documents will be maintained indefinitely following KDEP retention policies.
- Paper documents will be maintained by the project coordinator during the life cycle of the project, which will then be transferred to KDEP long term storage.
- Electronic files generated in the field via mobile devices will be transferred to KDEP servers and K-WADE as soon as possible after collection to avoid loss.
- Photography or video documentation of field conditions must document capture date.
- All born-digital and electronic copies will be maintained in the PFAS project files.
- Electronic files will be stored on KDEP servers offering back-up and recovery capabilities.
- Data will be entered into DOW's water quality monitoring database, Kentucky Water Monitoring Data for Environmental Assessment (K-WADE).
- Records filed in the project folders must have <u>initial data review</u> complete (i.e. staff name and review date must be in appropriate spot on form/datasheet) and may be released on request.
- Electronic files will follow standardized naming conventions, when applicable. Standardized naming of
 project documents allows end data users and personnel not affiliated with the project to easily find any
 document of interest.

1.5.1 QAPP and SOP

All original and revisions of the QAPP and SOPs will be distributed to project staff electronically prior to project initiation. The following guidelines apply to these documents:

- The Project Coordinator will facilitate review of QAPP documents and will oversee any necessary revisions with assistance from the DOW QAO.
- The DOW QAO will ensure that all approval signatures are completed on the QAPP and SOP in a timely manner to be available for integration into the QAPP for subsequent PFAS monitoring.
- Upon approval of the QAPP, the DOW QAO will file the QAPP and notify project coordinator, who will ensure the persons listed on the distribution list are aware of its location and availability.

1.5.2 Project Documentation and Records

This QAPP contains a list of all documents produced for the project, which serves as a checklist for the project coordinator to verify that records are complete and properly filed during project closeout. The documents and records for the project, listed in <u>Table 1.6</u>, include chain of custody (COC) forms, photographs, lab reports of analysis, equipment calibration and maintenance log, project QA tracking and summary, and the project final report.

Field records are produced during each station visit, with all information captured on the COC. Field records include monitoring station identification and location, date and time of sample collection, in situ field measurements, sampler names, number of sample containers and preservation methods, and pertinent comments. Lab records include all records related to receiving, processing, analyzing, and reporting sample results.

PFAS water samples are analyzed by the DEPS laboratory. The Project Coordinator receive results from the lab and reviews for errors. Data are then uploaded to K-WADE electronically via an export from the DEPS Laboratory Information Management System (LIMS) database, and are generally available to project staff within 2-4 weeks for routine samples.

QA/QC records include calibration and maintenance logs for instrumentation, documentation of QA/QC checks, data review checklists, and tracking forms for QA activities (<u>Table 1.6</u>). Project data reports are generated to provide updates to the project coordinator. Project final data reports include summaries of project outcomes and data reports extracted from the K-WADE database that are generated by the WQB QAC at the request of the data users.

1.5.3 Project Data

All project data will be entered into the K-WADE system, an Oracle-based database housed on KDEP servers. The project name will follow the convention "YYYY Program" where "YYYY" is the calendar year when field sampling commences. A new project is created in K-WADE for each sampling year unless it is a discrete project lasting less than two years. Field data are typically entered manually into K-WADE by activity leads from physical forms or are compiled into import templates for loading to the system. Analytical results for water samples submitted to DEPS are first entered into DEPS LIMS. On a periodic basis (typically weekly), results are imported to K-WADE for all samples that have been created in K-WADE by field personnel.

When project data review is complete (see <u>section 4</u>), the project coordinator approves the project, which then has all field activities and station visits marked complete before marking the project complete in K-WADE. Data from complete projects are included in the next submission to WQX, which will then be publically available via EPA's Water Quality Portal.

Table 1.6 Common documents that may be produced by DOW for this project. In the electronic filename template, the data should be entered in the following format "YYYY-MM-DD". When more than one document of a given type is completed for a visit, then they should be sequentially numbered. Photos must have

descriptions (e.g. upstream, left bank, substrate, species name, stressor type) at the end of the file name and/or in the attachment description in K-WADE.

Field Documents	Format	Electronic Filename Template
Site Photographs	JPEG or TIF	StationID_Date_Photo
Sample Chains of Custody	PDF	StationID_Date_COC
Laboratory Documents	Format	Electronic Filename Template
DEPS Sample Analysis Reports	PDF	StationID_Date_LabResults
QA/QC Records and Reports	Format	Electronic Filename Template
Equipment Calibration and Maintenance Log	Paper or XLS & PDF	Project Name Field Meter C-M Log
Project Data Review Checklists	XLSX & PDF	Project Name_QA Checklist
Project QA Tracking Sheet	XLSX/B & PDF	Project Name_QA Tracking Sheet
Project QA Summary	XLSB & PDF	Project Name_QA Summary
Project Final Data Report	DOCX or XLSB & PDF	Project Name_QA Checklist

2.0 DATA ACQUISITION

2.1 Sampling Design

This project is designed to meet three primary objectives:

- 1) Assess Kentucky's water resources for the occurrence of PFAS;
- 2) Extrapolate the risk of the occurrence of PFAS in Kentucky's water resources associated with various locations and facility types; and
- 3) Identify watersheds that have confirmed or potential PFAS contamination.

These objectives are being pursued using the following methods. The Department has selected stations for initial monitoring that are in proximity to areas and facilities that are known or suspected to manage PFAS. The location and frequency of additional monitoring sites will be determined based on results of the initial monitoring stations, as described later in this document. The Department anticipates preparing a report from this study that will include a summary and appropriate analysis of results, as well as any reasonable conclusions that can be made from these data.

An adequate sampling strategy must address the paucity of PFAS data in Kentucky's waters, with some level of focus on potentially problematic areas. As such, the Department has compiled locations of facilities that have the potential to manage PFAS as part of their normal operations. Because these chemicals are not currently regulated, there is no definitive listing of sites in Kentucky that store, use, or *potentially* discharge PFAS. Therefore, a systematic assessment of water resources is a reasonable approach to continue evaluating the occurrence of PFAS in Kentucky.

In addition, an adaptive approach to site selection and sampling frequency will allow for efficient data acquisition and strategic flexibility as the study progresses. The selection of sites for sampling is determined based on several factors that include the costs associated with sample collection and analyses, laboratory capacity, the rigorous sample collection protocols, data gaps left by the previous study, and locations of known and suspected facilities that manage PFAS.

This deterministic, yet adaptive, approach was utilized to develop the monitoring stations for this study, which will allow for coverage of waters across the state, with an emphasis on potentially problematic areas.

Furthermore, monitoring stations will be in key locations, such that results can be used to inform on the need for focused follow up investigations.

Using this approach, forty surface water stations have been selected due to their proximity to facilities that are known and suspected to manage PFAS. They represent various sized streams and rivers across Kentucky, along with the associated variation in drainage areas. The map in Figure 2.1 shows the proposed monitoring stations relative to major surface water drainages in Kentucky. Specific location details of the 40 sites are in Table 2.1, below. These sites are largely drawn from established surface water monitoring stations from various programs that happened to be located in the necessary stream reaches. A few of these sites were not previously established by other monitoring programs. All monitoring locations are subject to slight adjustment based on observations in the field and best professional judgement of the sample collectors. It is recommended that each of these sites be sampled once in an initial round of monitoring. Results of this first round of monitoring can then be assessed to determine if repeat sampling is necessary at a particular site, or if additional sites should be included to better evaluate the geospatial occurrence of PFAS in Kentucky's waterways. Repeat sampling will also allow for sites to be sampled under varying flow conditions.

The results of the initial samples collected at the 40 targeted sites will be evaluated to determine where additional sampling should occur. These results will be reviewed as they are received from the laboratory and evaluated in regards to the area land use and facility types that influence water quality at each monitoring station. All sample results for the initial round of monitoring will be reviewed and evaluated by the project coordinator and Department management prior to determining the appropriate approach for additional monitoring. Several options are available to select these additional monitoring locations, which are discussed below.

Repeat samples at some or all of the initial monitoring locations could be utilized to address seemingly elevated PFAS concentrations, or to build a more robust dataset. Follow up monitoring at initial sites would help to capture temporal variations in PFAS concentrations, and may also capture changes in flow regime. These repeat samples could also include monitoring stations located upstream and/or downstream of the initial sample site to provide clarification of results. Long-term, site specific investigations deemed necessary would be excluded from this study and conducted independently.

Additional targeted locations may be selected based on the results of monitoring stations in proximity to particular industry types. If the initial round of samples indicates that certain industries or facility types are more likely to be associated with PFAS detections, then the focus of additional monitoring could turn to those types of locations. Sample site selection (location and surface water or groundwater station) would be based on the hydrogeologic setting surrounding the facilities of interest.

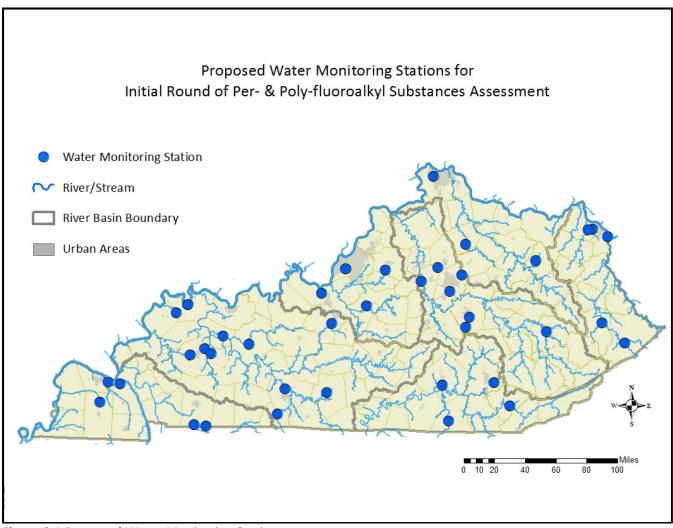


Figure 2.1 Proposed Water Monitoring Stations

 Table 2.1.
 Monitoring stations selected due to proximity to potential PFAS sources

LOCATION NAME	MAJOR RIVER	COUNTY	LATITUDE	LONGITUDE
Levisa Fork	BIG SANDY R	Floyd	37.601790	-82.700570
Levisa Fork	BIG SANDY R	Pike	37.406980	-82.443260
Big Sandy River	BIG SANDY R	Boyd	38.414839	-82.596659
Buck Creek	GREEN R	McLean	37.505340	-87.197210
Muddy Creek	GREEN R	Ohio	37.434840	-86.885780
West Fork Drakes Creek	GREEN R	Simpson	36.773900	-86.541900
South Fork Beaver Creek	GREEN R	Barren	36.980640	-85.968190
Valley Creek	GREEN R	Hardin	37.638846	-85.907748
Elk Creek	GREEN R	Hopkins	37.385670	-87.412250
Pond River	GREEN R	Muhlenberg	37.338260	-87.334770
Barren River	GREEN R	Warren	37.015086	-86.459823
North Elkhorn Creek UT 66.0	KENTUCKY R	Fayette	38.085800	-84.356100
Bailey Run	KENTUCKY R	Anderson	38.032940	-84.843160
Harts Fork	KENTUCKY R	Madison	37.686046	-84.273745
North Fork Kentucky River	KENTUCKY R	Breathitt	37.531480	-83.364270
South Elkhorn Creek	KENTUCKY R	Woodford	38.160300	-84.643900
Walnut Meadow Branch	KENTUCKY R	Madison	37.593586	-84.324318
West Hickman Creek	KENTUCKY R	Jessamine	37.934467	-84.502258
North Fork Triplett Creek	LICKING R	Rowan	38.209895	-83.467157
South Fork Licking River	LICKING R	Harrison	38.376670	-84.304170
East Fork Little Sandy River	LITTLE SANDY R	Greenup	38.492874	-82.779083
Little Sandy River	LITTLE SANDY R	Greenup	38.490460	-82.834180
West Fork Red River	LOWER CUMBERLAND R	Christian	36.651642	-87.377656
Quarles Spring Branch	LOWER CUMBERLAND R	Christian	36.664020	-87.525240
Mayfield Creek	MISSISSIPPI R	Graves	36.852060	-88.633810
Casey Creek	OHIO R	Union	37.718880	-87.757100
Canoe Creek	OHIO R	Henderson	37.802000	-87.624800
Otter Creek	OHIO R	Meade	37.923600	-86.030300
Gunpowder Creek	OHIO R	Boone	39.026650	-84.678710
Canoe Creek	OHIO R	Henderson	37.802000	-87.624800
Brashears Creek	SALT R	Shelby	38.139143	-85.295981
Beech Fork	SALT R	Nelson	37.396641	-85.480542
Duck Spring Branch	SALT R	Jefferson	38.153660	-85.742200
Cypress Creek	TENNESSEE R	Marshall	37.033300	-88.401900
Clarks River	TENNESSEE R	McCracken	37.046790	-88.543119
Greasy Creek	TRADEWATER R	Hopkins	37.324400	-87.585100
Big South Fork Cumberland River	UPPER CUMBERLAND R	McCreary	36.702800	-84.534700
Laurel River	UPPER CUMBERLAND R	Laurel	37.059510	-83.998800
Sinking Creek	UPPER CUMBERLAND R	Pulaski	37.045523	-84.603462
Cumberland River	UPPER CUMBERLAND R	Knox	36.835800	-83.811980

Additional monitoring stations could be selected based on the need to address geospatial data gaps. For efficiency, these potential additional monitoring stations could be drawn from the Ambient Rivers Monitoring Program and Ambient Groundwater Monitoring Network. However, it may be more appropriate to select stations that have not been previously established. This decision will be based on an assessment of the initial round of monitoring and identified needs for improved spatial, temporal, and flow regime evaluation.

The adaptive approach would also allow for additional monitoring stations to be selected via a random, probabilistic draw to obtain unbiased sampling locations. The list of randomly drawn monitoring stations would come from existing probabilistic monitoring site lists. However, a determination of the stream population of interest (headwaters, wade-able or boat-able) would need to be made.

One final consideration would be the addition of fish tissue analyses by a contract lab. PFOS is known to bioaccumulate in fish tissue, which can be a public health concern for those who consume fish from Kentucky's waters. A number of states currently have fish consumption advisories due to PFOS, but Kentucky does not yet have the lab capability to analyze for PFAS in tissue. Consequently, the only data available on PFAS concentrations in fish in Kentucky may be from EPA's 2008-2009 National Rivers and Stream Assessment where a two-fish composite sample collected from the Ohio River downstream of Owensboro was found to have a concentration of $34.1 \,\mu\text{g/L}$ of PFOS and an estimated concentration of $2.6 \,\mu\text{g/L}$ for perfluoroundecanoate (EPA 2009).

In addition to increasing the data available on concentrations of PFAS in fish in Kentucky, fish tissue analysis is also beneficial in identifying the presence of contaminants that may flush through a waterbody only periodically and consequently be challenging to catch with a single water sample. If tissue analysis is pursued during this study, it would require additional personnel from the Water Quality Branch with expertise in fish sample collection. There are no additional fish processing or shipment considerations for PFAS outside of normal DOW protocols.

Following the initial sample collection at all 40 targeted sites and the evaluation of data obtained, an interim report will be produced to document findings. This interim report will include a discussion of the data evaluated and the decision making process regarding how and where additional sampling shall occur.

2.2 Sampling Procedures and Requirements

Field sampling and laboratory analysis procedures have been developed into SOPs. Details for sample requirements such as holding time, preservatives, and sample volumes for chemical analyses performed by DEPS can be found in Appendix L of the DEPS LOQAM. Site specific activities include collection of samples for non-potable water PFAS analysis method, collection of samples for drinking water PFAS analysis method, *in situ* water quality measurements, and completion of the COC form.

Three approaches may be employed for PFAS water data collection depending upon the station characteristics and sampler safety concerns. These include direct stream grab samples, bank sampling, and bridge sampling. Water samples will be shallow grabs, at minimal depth to avoid potential cross contamination of the sample collector. If feasible, *in situ* measurements will be collected at mid-depth when the water depth at the sample location is ≤ 10 feet. If the water depth is > 10 feet or it is not feasible to measure the depth, *in situ* measurements will be collected at a depth that is deemed reasonable by field staff. PFAS samples should be collected regardless of flow level, provided that there is at least perceptible flow present and samples can be collected safely. Flow conditions and depth of *in situ* measurements shall be noted on the COC. In this project, PFAS data are critical; all other data are for informational purposes only.

At each monitoring station samples will be collected for analysis using both the Non-potable Water PFAS Analysis Method (SW 846 Method 8327) and the Drinking Water PFAS Analysis Method (Method 537.1). Collection materials and methods are documented in DEPSOP001, Sampling Procedures for Per- & Poly-fluoroalkyl

Substances. The primary analysis method will be the Non-potable Water PFAS Analysis Method. However, the method detection limit for this analysis is 20-40 ng/L, which is an order of magnitude higher than those for the Drinking Water PFAS Analysis Method. The DEPS lab has successfully employed both analysis methods for surface water samples. If the results of the Non-potable Water Analysis Method show analyte detections then further analysis by the Drinking Water Analysis Method with lower method detection limits will not be necessary. If the results of the Non-potable Water Analysis Method show all analytes not detected, then the samples collected for the Drinking Water Analysis Method will be analyzed to determine if PFAS are present at lower concentrations.

2.2.1 Water Sample Collection

Direct in-stream grab sampling (wading) is the preferred method for collection of PFAS water samples. With this method the sampler approaches the sample station from a downstream location. Samplers should take care not to disturb bottom sediments that could contaminate the sample. An ideal wading location is at the head of a riffle so that water current produces a good flow past the sampling point. Samplers should ensure that the sample location is well-mixed and representative of the stream or river at the sample station.

Bank sampling is acceptable when wading is not feasible. When bank sampling, it is important to make sure that the water at the point of sampling is well-mixed and representative of the stream. If the channel configuration and/or flow is such that the water is well mixed throughout the stream width, then bank sampling is appropriate. If the water near the bank is somewhat isolated from the main flow of water, then use of a swing sampler will be necessary to retrieve the sample from farther out in the channel.

Bridge sampling is used only when stream depths or access prevent in-stream sampling. A weighted bottle sampler is the method of choice if sufficient room is available on the bridge to sample safely without any disruption to the flow of traffic. Effort should be made to avoid bridge sampling when possible, by locating an alternate stream access location in close proximity.

2.2.2 Collect *In situ* Water Quality Measurements

Prior to each sampling trip the *in situ* multi-parameter sonde must be calibrated. At each station it is important to collect these measurements last, so as to reduce the probability of sample contamination. An in situ multi-parameter sonde is used to collect temperature, pH, conductivity, and dissolved oxygen data. While these data will be collected at each monitoring station, they are for informational purposes only.

2.2.3 Complete Chain of Custody Form

A COC must be completed for each sampling location. The required information includes the station identifier and location, date and time of sample collection, *in situ* field measurements, and the number of sample containers with preservation methods. The COC also has a comments section, which is to be used to indicate any ancillary information deemed pertinent by the sample collectors. An example of the COC is located in the appendix.

2.2.4 Photo Documentation

Photo documentation may be collected at monitoring stations, if deemed necessary by field staff. Reasons for photo documentation may include sites with difficult access, documenting sampling locations relative to stream channel morphology, or to document other field observations. However, not all sites will require photo documentation of the sampling location.

Category	Subcategory	Standard Operating Procedure Title	
Physical/Chemical	PFAS Sampling	Sampling Procedures for Per- & Poly-Fluoroalkyl Substances	
	In situ Multi-Parameter Meters	In-situ Water Quality Measurements and Meter Calibration for Lotic Waters	

Table 2.2. Field standard operating procedures

2.3 Sample Handling and Custody Requirements

A sample is in "custody" if it is in the actual possession of a sampler or in a secured area that is restricted to authorized personnel. Once a sample is in the custody of DOW staff, guidelines for storage and transport from the SOP (Table 2.2) will be followed including COC requirements and sample holding times (see Appendix L of the DEPS LOQAM or applicable SOPs for holding time information). The DEPS lab also provides a comprehensive list of handling and custody requirements for water chemistry samples in Appendix L of the DEPS LOQAM. The COC used in this project will include the following:

- 1. K-WADE Station Identifier;
- 2. Date and Time of Sample Collection;
- 3. Site description/location description;
- 4. Project Name;
- 5. DEPS Program Code (DEPS-submitted samples);
- 6. Media of sample;
- 7. Collection Method Type (e.g., grab) and Sample Depth;
- 8. Analyses Requested;
- 9. Number of Containers;
- 10. Preservation; and
- 11. Signature/Date/Time Blocks for relinquishment of samples.

2.4 Analytical Methods Requirements

Analytical methods include non-potable water PFAS analysis and drinking water PFAS analysis. The non-potable water PFAS analysis will be the primary tool to evaluate the occurrence of this class of chemicals in Kentucky's water resources. However, samples will also be collected for analysis using the drinking water PFAS method (537.1) because detection limits are an order of magnitude lower than the non-potable analysis method. The DEPS laboratory will only analyze samples using the drinking water PFAS method if results of the non-potable water PFAS method are all non-detections. Laboratory procedures and requirements will follow SOPs. These SOPs follow methods approved by the EPA, as listed in the Federal Code of Regulations (CFR) 40 CFR Part 136.

The analytes that will be reported by the DEPS lab for this project are listed in Table 2.3. Laboratory staff are responsible for ensuring that method requirements are met and for informing project coordinator of deviations so corrective actions can be taken.

Chemical analyses are performed at the DEPS lab following the <u>DEPS LOQAM</u> and SOPs (<u>Table 2.2</u>). Detection limits of each analysis are based on instrumentation and laboratory capabilities. Specific information on methods for analytes including Limit of Detection (LODs) and Limit of Quantification (LOQs) can be found in the <u>DEPS schedule of services</u>, and are summarized for PFAS being evaluated in this project in <u>Table 2.3</u>. The DEPS manager will communicate any planned changes to methods or limits to program supervisors. Analytical results will be delivered to the project coordinator electronically as they are verified by the DEPS manager, which is generally within 21 days maximum turnaround time.

Table 2.3. Methods, detection limits, and reporting limits for PFAS¹.

Parameter (Acronym)		LOQ	LOD	Lab SOP Water	Unit
PFAS Non-Potable Water Method:					
Perfluorobutanesulfonic acid	(PFBS)	80	40	\$6060	ng/L
Perfluoroheptanoic acid	(PFHpA)	80	40	\$6060	ng/L
Perfluorohexanesulfonic acid	(PFHxS)	80	40	\$6060	ng/L
Perfluorononanoic acid	(PFNA)	80	40	\$6060	ng/L
Perfluorooctanesulfonic acid	(PFOS)	80	40	\$6060	ng/L
Perfluorooctanoic acid	(PFOA)	80	40	\$6060	ng/L
4,8-dioxa-3H-perfluorononanoic acid	(ADONA)	40	20	\$6060	ng/L
Hexafluoropropylene oxide dimer acid	(HFPO-DA)	80	40	\$6060	ng/L
PFAS Drinking Water Method:					
Perfluorobutanesulfonic acid	(PFBS)	3.54	1.18	\$6065	ng/L
Perfluoroheptanoic acid	(PFHpA)	2.89	0.964	\$6065	ng/L
Perfluorohexanesulfonic acid	(PFHxS)	2.89	0.964	\$6065	ng/L
Perfluorononanoic acid	(PFNA)	2.89	0.964	\$6065	ng/L
Perfluorooctanesulfonic acid	(PFOS)	2.89	0.964	\$6065	ng/L
Perfluorooctanoic acid	(PFOA)	2.89	0.964	\$6065	ng/L
4,8-dioxa-3H-perfluorononanoic acid	(ADONA)	2.89	0.964	\$6065	ng/L
Hexafluoropropylene oxide dimer acid	(HFPO-DA)	3.54	1.18	\$6065	ng/L

¹ Sampling guidelines (i.e. minimum volumes, container types, preservatives and holding times) for all samples collected can be found in <u>Appendix L of the DEPS LOQAM.</u> All Laboratory SOPs are available upon request.

2.5 Quality Control Requirements

Monitoring staff are responsible for ensuring that all field (Table 2.4) QC requirements are completed accurately and on time. All monitoring stations will be sampled in duplicate for each of the analysis methods (Non-potable and Drinking Water methods), per the DEPS lab request, and one randomly chosen station will be sampled in triplicate on each sampling day. Additionally, a Trip Blank of PFAS-free water will accompany each cooler used for sample preservation on every sampling trip. These stringent QC requirements are due to the sensitivity of laboratory analyses and ubiquitous nature of the analytes being evaluated. Refer to Table 1.5 for QC sample acceptance criteria.

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For samples analyzed by the DEPS, DEPS staff members are responsible for ensuring that all QC requirements for each program are completed accurately and on time. QC samples for DEPS are explained in all laboratory SOPs (Table 2.2), and/or in the laboratory's LOQAM.

2.6 Testing, Calibration and Maintenance Requirements for Equipment and Supplies

2.6.1 Instrument Testing and Instrument Calibration

The project coordinator is responsible for the testing and calibration of all electronic sampling equipment, including multi-parameter water quality probes. Calibrations will occur at least with the frequency recommended by manufacturer specifications and SOPs for each water quality parameter (<u>Table 2.4</u>). A log will be kept for each instrument tracking calibration activities. The calibration records will include the date and time of calibration, the equipment serial number, and the pre- and post-calibration values for each parameter calibrated.

Maintenance supplies and spare parts for instruments will be kept in the field storage building (150 Sower Blvd).

 Table 2.4. Summary of field sampling quality control requirements utilized in this project.

Requirement	Frequency	Corrective Action	Persons Responsible for Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Water PFAS Field Duplicates and Triplicates	Duplicates collected at 100% of sites. Minimum of 10% of samples collected in triplicate, distributed across the project	Evaluate and compare lab dups Qualify data as necessary	Project Coordinator	Precision	≤20% RPD if both original and replicate samples are ≥ five times (5x) the Limit of Quantitation (LOQ), otherwise see <u>Table 1.5</u> .
Water PFAS Trip Blanks	One for each field sampling cooler	Qualify data as necessaryReview sample collection and storage procedures	Project Coordinator	Precision, Accuracy, Bias	< LOQ
Water PFAS Field Blanks	One for each site	Qualify data as necessaryReview sample collection and storage procedures	Project Coordinator	Precision, Accuracy, Bias	< LOQ
Calibration of water quality probes and data sondes	Prior to each day of use	•Re-calibrate to within allowable specs.	Project Coordinator	Accuracy	Must meet or exceed instrument accuracy specs. (Table 1.3)

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A list of all DEPS instrumentation can be found in <u>the laboratory's LOQAM</u>. This document also describes all of their testing and instrument calibration protocols.

2.6.2 Supplies and Consumables

All supplies and consumables used for this project will come directly from the DEPS laboratory and will be certified as PFAS-free materials. Sampling containers include 15 mL High-density polyethylene (HDPE) vials and 250 mL HDPE wide-mouth bottles. Powdered TRIZMA™ is used to preserve samples collected for the drinking water PFAS analysis method. The DEPS lab supply manager is responsible for maintaining proper documentation for supplies (e.g. recording lot numbers and expiration dates), inspecting supplies upon receipt, discarding expired supplies, and reporting to the Branch QAC and Division QAO of results of any problems and corrective actions. It is the project coordinator's responsibility to communicate supply needs to the DEPS lab supply coordinator.

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All reagents and standards are traceable to the manufacturer lot number and Certificate of Analysis (COA). Further details on QA/QC of DEPS lab supplies and consumables can be found in the DEPS LOQAM.

2.7 Data Acquisition Requirements for Non-direct Measurements

Non-direct measurements include data obtained from existing data sources; these data are not directly measured or generated from the project. Throughout all monitoring programs implemented in the DOW, there are many common types of non-direct measurement data that are often used. Unless specified otherwise, all non-direct data are considered non-critical and used for informational purposes only. These data sources include:

GIS Analysis

Review of all project areas is performed through GIS analysis as part of the process of drafting study plans. Information obtained from GIS will be verified during reconnaissance when possible. All data obtained from GIS will be referenced as such in all reports.

National Permitted Discharge Elimination System - Permit Limits and Facility Compliance History

The <u>Integrated Compliance Information System (ICIS)</u> is used to compile permit information including design flow and pollutant limits. <u>The Enforcement and Compliance History Online (ECHO)</u> interface is used to compile compliance history for National Pollutant Discharge Elimination System (NPDES) permitted facilities.

Weather/Climatic Data

Precipitation data, forecasts, and radar from National Centers for Environmental Information, Kentucky Mesonet, and Weather Underground, are often used to identify potential runoff events. This information can be used to target or avoid stormflow events. However, there are limitations on the effects that weather can have on local conditions. Data from United States Geological Survey (USGS) hydrologic data from real-time gaging stations may also be used to determine discharge conditions (stormflow, base flow, low flow). Gaging station data are limited by the number of stations in the state and many stations are being discontinued due to lack of funding.

Limitations of Non-direct Measurements

Any data obtained by means of non-direct measurement will be flagged as such in all final data reports. These data should be used with discretion, as they will not be validated.

2.8 Data Management Requirements

After initial data review and data entry, project coordinators are responsible for ensuring that data are entered into K-WADE, and that project documents are stored properly in both K-WADE and on network drives. The WQB Branch Manager will coordinate on data verifications and QA procedures, and assign secondary QA tasks to promote independence between data generation and QA/QC of data. Finally, the project coordinator will ensure that all data entry verifications and validations are complete before authorizing a project and its components to be marked complete (see Section 4).

With a few exceptions, data are stored in K-WADE, and retained indefinitely. K-WADE is a web-interface to an Oracle database with modern security features. Unique station identifiers are created for all locations where field data are collected following the <u>K-WADE Monitoring Station Creation SOP</u> (DOWSOP03038, 2015). After projects are marked complete, data are locked for edits and must be unlocked by an administrator. K-WADE's reports tool creates data reports in standard formats. Data from complete projects are submitted from K-WADE to WQX by KDEP Information Technology (IT) staff via KDEP's exchange network node.

Field data are recorded on physical field forms and entered directly into K-WADE or in some cases into an intermediary K-WADE upload template.

Laboratory results for samples submitted to the DEPS laboratory are processed using the LabWorks® system, external spreadsheets, or manual calculations. Data are also processed and validated through the DEPS LIMS. LIMS is used for final review of all data and for final report generation. LIMS results are imported into K-WADE automatically once project coordinators create the sample in K-WADE and enter its metadata. The K-WADE import process checks the station identifier and verifies date and time match between LIMS and K-WADE before import.

The following practices will be maintained for all data management activities:

- Electronic files will be transferred to KDEP servers and attached in K-WADE as soon as possible to avoid loss.
- Original versions of electronic files will be retained even if files will be annotated or processed.
- Data will be entered or uploaded to K-WADE as soon as practical to avoid loss.
- Manual data entry will be checked for accuracy (minimum 10%) by a second independent staff member designated by the project coordinator.
- Data imports, uploads, and transfers will be checked (minimum 5%) for systematic transfer errors.
- Data processing templates or coded scripts (e.g. in R or SAS) will be write-protected to avoid accidental changes; calculations derived from scripts will be checked at a rate of at least 5%.
- All monitoring data will be entered into K-WADE. Exceptions may include indirect measurements
 used for informational purposes (e.g. USGS gage data) or data types or monitoring designs which KWADE does not yet accommodate.
- Data that cannot be entered into K-WADE will be stored in project files.
- Paper and electronic data forms will be uploaded as PDF attachments during data entry and/or upload.

3.0 ASSESSMENTS AND OVERSIGHT

Project assessments are designed to determine whether the QAPP is being implemented as approved, and ultimately to ensure that the information will be usable for the intended purpose. The project coordinator is responsible for coordinating assessments throughout project cycles for implementing corrective actions. Generally, assessments are conducted at the project level. Assessment results are conveyed via regular meetings between the project coordinator and KDEP management.

3.1. Project-Level Assessments and Response Actions

All activities are tracked by the project coordinator and recorded in electronic data reports, which are distributed periodically (generally at least bi-weekly during the field season, but as frequent as weekly), and stored on KDEP servers. The project coordinator will use the tracking information to report monthly on project status to KDEP management and to ensure that tasks are on schedule.

The project coordinator is responsible for reviewing project activity metadata and data reports to ensure that collection methods and analyses are being implemented as planned, and that all data appear complete and correct in K-WADE. These reviews will be accomplished by reviewing field and lab documents, periodic data reports provided by the WQB QAC, or via K-WADE reports as appropriate. The project coordinator must report when deviations from QAPP requirements occur, and notify the DOW QAO.

The project coordinator tracks the progress of data entry and QA/QC tasks via periodic K-WADE reports. The K-WADE "Project Field Activity" and "Project Station Visits" reports show dates of data entry, Field Activity QA completion, Station Visit closeout, and Project closeout. K-WADE "Sample Results" and "Field Measurements and Observations" reports can also be used to review data.

The project coordinator has the responsibility of ensuring that data from DEPS are consistently of a documented and usable quality. This is done by reviewing lab reports for errors, inconsistencies, and/or poor QC results, and also via communication with lab staff. A corrective action request must be submitted to the DEPS Laboratory Technical Director for all laboratory deviations and deficiencies. All Corrective Actions submitted to DEPS will follow the procedures outlined in the <u>DEPS LOQAM</u>. All related documents will be maintained as described in this QAPP.

3.2. Program-Wide Assessments and Response Actions

Project data reports are run regularly from K-WADE to monitor the status of any issues or corrective actions. Issue resolution may involve examining the condition of supplies, arranging staff re-training on procedures, or working with lab staff to address possible analytical issues.

The project coordinator will conduct regular assessments of QC blank results, QC replicate comparisons, and lab analysis flags to ensure that data quality issues with field or analytical methods are identified in a timely manner. These assessments are conducted at least monthly using the project data reports. The project coordinator will report the results of these assessments to KDEP management for review. If necessary, the WQB QA/QC workgroup will meet to discuss issues.

Project personnel may be subject to audits by the WQB QAC, DOW QAO or designees at any time during or after the close of a project. Audits may include review of calibration logs, field and laboratory documents, tracking sheets, or performance testing samples for field measurements.

Final project QA data reports are reviewed to identify program-wide or project-specific QA/QC issues that may affect data usability for current or future uses. The WQB QA Workgroup will work with the Division QAO to recommend cross-program or program-specific remedies for issues that are identified.

4.0 DATA VERIFICATION, VALIDATION AND USABILITY

The project coordinator and WQB QA staff are responsible for performing verification and validation tasks. Verification and validation checklists (see <u>Section 4.2</u>) are used to ensure similar QA effort across programs. Completion dates of key review steps and the person who performed the review are recorded in K-WADE.

Evaluations of data usability are done in coordination with data end-users, such as DOW and KDEP management. Data validation results and usability qualifiers/comments are transmitted to data users in standard reports to ensure that usability considerations are understood and documented.

4.1 Data Review, Validation, and Verification Criteria and Documentation

When data do not meet the specifications required in this document the data are qualified so that they can be reviewed for usability by data end users. Data qualifiers are entered into K-WADE so that any qualifiers present in the data are easily found in Project Data Reports extracted and compiled from K-WADE. Reasons for absolute rejection of field data could include significant alterations to procedures, use of expired supplies, failure to calibrate instrumentation, or failure to positively identify the sampling location. Reasons for absolutely rejecting laboratory results could include exceedances of holding times, improper sample preservation and handling, significant alterations to procedures, or failure to calibrate laboratory instrumentation.

Reporting of all data collected, with qualifiers where necessary, is ideal so that end data users can make decisions on usability. For example, a holding time exceedance may render data unusable for the project final report, but the data could still be useful in screening to prioritize sites for follow-up monitoring. The DEPS laboratory uses a standard set of qualifiers for analytical results. The flags, their meanings, and the guidelines for applying flags are described in the <u>DEPS LOQAM</u> with all flags descriptions being found in <u>Appendix O</u>. Data qualifiers for field data are recorded in the form of comments at the field activity level. Data qualifiers for biological results are recorded in the form of comments at the sample or result level as appropriate.

4.2 Validation and Verification Methods

Data validation and verification uses a standard set of checklists at four key steps in the data collection and management life cycle, as described below.

4.2.1 Initial Data Review

Initial data review refers to verification checks performed immediately following field activity completion (e.g., prior to leaving the site, or upon completion of a laboratory task), upon receipt of the DEPS sample login confirmation email, or upon receipt of the laboratory analytical results from DEPS (PDF delivered via email). This review is typically done by the project coordinator upon receipt of the datasheet. This review must be performed prior to filing documents in physical files, creating scanned backups of physical files,

or filing electronic files in project folders. Initial data review is acknowledged as completed by placing the name of the reviewer and the review date in the appropriate datasheet locations.

Any errors must be resolved as soon as possible to ensure that they do not become propagated in databases or other permanent records. Laboratory analysis issues uncovered during initial data review can sometimes be resolved by re-analyzing if the review is done promptly. After initial data review, records are filed and data entry into K-WADE is arranged. All data and records generated by this project will be considered preliminary and, thus, not discoverable by means of an open records request until all project closeout procedures outlined in the work plan and this QAPP are complete, and the project is marked complete in K-WADE. The only exception to this is final lab reports of analysis that have undergone full laboratory QA/QC procedures, which will be discoverable upon receipt by DOW. Initial data review is divided into four sequential categories occurring throughout the data collection and review process, including:

Post-field activity checks:

- Field forms are completely filled out and are legible.
- All required measurements and observations have been made, all samples taken, and all pertinent visit/activity comments have been recorded.
- All forms have correct date and accurate activity times; when multiple activities are coordinated at a visit, ensure that the visit start time is recorded appropriately.
- Sample COCs are complete and samples properly preserved.
- Station identifiers match site list and the correct location has been visited.
- Measurements are within a reasonable range; add comments to sample activity in K-WADE where anomalies are apparent.

DEPS lab sample login confirmation check:

- Sample date, time, and sample type logged into LIMS match what is on COC.
- Sample assigned to correct program reporting code and correct analytes requested.

Lab sample results (DEPS):

- Sample date, time, and sample type are correct.
- Results are within expected ranges; add activity comments in K-WADE where anomalies are apparent.

4.2.2 Field Activity QA

Field activity QA refers to verification and validation performed at the activity level (e.g. individual sets of samples, sets of measurements, biological sample collections performed at a visit). In K-WADE the completion of these checks are recorded as primary and secondary QA, along with the person performing the check and the date of completion. The project coordinator ensures the completion of Primary QA on all activities. Primary QA is completed to check for exceptions to QAPP requirements for field and lab procedures and to ensure that qualifiers and comments are recorded where exceptions occur. This review also includes comparison of QC samples to QAPP requirements and examining result values for anomalies. Secondary QA is performed for a portion of or all visits (minimum 10% of all activities), consisting of checks on manual data entry or data uploads. Since secondary QA is an audit of data entry, a staff member that was independent of the data collection and data entry completes this task. A set of checklists for each activity type are used to guide these checks and to facilitate compiling notes for later compilation into the final Project Data Report (Table 4.1), which can be provided to end data users for making decisions on data usability for their specific purpose. Primary and Secondary QA are marked complete after review.

4.2.3 Station Visit Review and Visit Closeout

Station visit review refers to verification and validation performed at the visit level (sets of activities performed at a location within a specified time-frame). The project coordinator completes <u>the station visit checklist</u> once data results for all activities have been entered and primary and secondary QA have been completed. This review consists of checking that all activities were completed, that all field instruments used are traceable to calibration logs, and that comments recorded for the visit or activities are clear. Following station visit review and approval, the station visit can then be marked complete in K-WADE.

Table 4.1 Field activity QA validation and verification methods employed by the KY Division of Water.

Checklist	Description		
Sample Collection Checklist	Water PFAS sample collection and analysis QA checklist		
Field Measurements and	Checklist for Field Measurement and Observation Forms		
<u>Observations</u>	Checklist for Field Measurement and Observation Forms		

4.2.4 Project Level Review and Project Closeout

Project-level review refers to the verification and validation performed at the project level (sets of visits conducted for a project). The project coordinator will verify the completion of the project-level review and project closeout checklist after all visits have been marked complete. This review consists of checking that all visits have been entered, all documents have been filed according to QAPP requirements, and that the project metadata are complete in K-WADE. A final project data report is generated that consolidates and summarizes results from field activity and station visit review (Sections 4.2.2 and 4.2.3). This report contains all of the finalized data generated by the project along with any data qualifiers, and the results of the primary and secondary QA completed on the project, which details any QA/QC and data usability issues for the project. The final project data report will be submitted to the project coordinator, who then reviews the report and approves marking the project complete in K-WADE.

4.3 Reconciliation with Project Requirements

Data usability considerations are communicated to data end users through the final project data reports, which summarize data quality issues and annotate data with appropriate QA qualifiers. In addition, data reports run from the K-WADE reports tool contain all data qualifiers and comments. Any custom queries and reports must also include these qualifiers.

The project coordinator and WQB Manager will review the final project data summary report and will make final decisions on usability. Data usability will be determined based on meeting the requirements to achieve the primary project objectives outlined in Section 2.1. Data must be of sufficient quality to determine the presence or absence of PFAS at monitored locations. These data will be used to determine the relative risk of PFAS occurrence in Kentucky's waterways associated with various land use and facility types. Data must also be of satisfactory quality to determine if PFAS contamination has occurred within any of the watersheds with monitoring stations.

The project coordinator will work with the WQB Manager and QA staff to make necessary modifications to procedures and program/project design in order to maximize data usability. The project coordinator will also work with the WQB QAC to ensure that QA/QC and reporting procedures provide the necessary data and information to make confident and objective decisions on data usability. In addition, the WQB Manager will solicit feedback from other data end users regarding usability of monitoring project data.

5.0 REFERENCES

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Appendix – Example Chain of Custody

CHAIN OF CUSTODY RECORD ENERGY and ENVIRONMENT CABINET DIVISION OF WATER KENTUCKY PFAS PROJECTS – A70

Site Identification			Collection Date/Time	Field Parameters Reading Depth:		
Field ID:				Date:	pH:	
					Cond (µS):	
Stream Name:			Time:	·		
Location:					Temp (°C):	
County:					DO:	mg/L /%
Lat: Long:				Flow Est (f	t ³ /s):	
				Meter ID: Calibration	Date:	
					Canoration	Dute.
Sampler ID:_		Division of F	nvironme	ontal Program Suni	nort	
Number of	Container	Preservation Preservation	II VII OIIIIC	nvironmental Program Support		DEDC Comple #
Containers	Size, Type	Method	***	Parameters	DEPS Sample #	
	250 ml HDPE	1.25 g Trizma Cool to 4°C	PI	FAS – Drinking Water Me	thod	
	250 ml HDPE	1.25 g Trizma Cool to 4°C		Field Blank Analysis		
	15 mL HDPE Vial	Cool to 4°C	PFA	AS – Non-potable Water M		
Signatures:						
Relinquished by:						
Received by:				Date:	Time:	
Palinguished by						
				Date:	Time:	
Received by.						
COMMEN'	TS:					
*Note here	if site sample	d in Triplicate	•			

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PFAS Phase II QAPP

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